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Beyond water splitting - efficiencies of photoelectrochemical devices producing hydrogen and valuable oxidation products

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The majority of studies on cathodic photo-electrochemical (PEC) hydrogen production consider water oxidation (yielding oxygen) at the anode. Oxygen is not only a non-valuable product, it also requires significant over-potential to be formed. In this perspective communication, results of theoretical calculations are presented providing tandem PEC efficiency limits for alternatives to anodic water oxidation, showing that valuable oxidation products can be produced efficiently in solar-to-hydrogen devices.

Seasonal fluctuations in renewable energy production have stimulated investigation of approaches to photosynthetically produce fuels, such as hydrogen.[1–3] These so-called solar fuels need to be scalable to the terawatt level, and therefore the considered co-product of fuel is usually oxygen.[1–5] Since oxygen has negligible economic value, an attractive alternative approach would be to produce value-added oxidation products.[6,7] Production of

economically favorable products (see **Table 1**) or waste streams,[8] might considerably reduce time to market of photo-electrochemistry (PEC)-based devices.

Oxidation of halides is an interesting alternative for oxidation of water. Anodic conversion of halide-containing salts (NaCl, KBr), or acids (HCl, HBr) leads to gaseous products (i.e. Cl_2, Br_2). Chlorine is typically used to make PVC, or is used in the production of pharmaceuticals. Cl_2 is already produced commercially via electrolysis, thus the fundamental knowledge for PEC chlorine electrolysis is already established. The annual production of chlorine is the equivalent of 0.2 TJ worth of H_2 storage. While this amount is insufficient for world-wide energy storage requirements, it is still significant. Bromine is frequently used for production of chemical intermediates and its production has already been considered by Texas Instruments using PEC based devices.[9] Various other researchers have evaluated this path more recently.[10,11] Hydrogen peroxide is another interesting product, due to its economic value. It is used as disinfectant, bleach or soft oxidant. While industrially H_2O_2 is produced using the anthraquinone oxidation process,[12] it is also well known that H_2O_2 can be produced via electrochemical oxygen reduction.[13,14] Finally, H_2O_2 can be produced via electrochemical oxidation of water, albeit at relatively low faradaic efficiency, due to competitive O_2 production. For carbon-based electrodes, efficiencies of 30-50% have been reported.[15] Additionally, oxides such as MnO_x appear promising catalysts.[16,17] Table 1 shows that the current market price of the mentioned alternatives is significantly more attractive than oxygen.

The material requirements (e.g. corrosion resistant's) and the techno-economic viability of these devices should share many of the same traits as reported for PEC water splitting.[18–20] Since all of the aforementioned reactions are simple 2e- oxidation reactions with minimal overpotential, losses due to scaling relations should be less important than encountered in water oxidation.[21,22]

PEC systems for water splitting[23,24,11,25–28] have been extensively modeled, and to a lesser extent PEC systems for CO_2 reduction.[29,30] To the best of our knowledge, an in-depth modeling of halide oxidation, or oxidation of water to H_2O_2, has not yet been published. In this perspective, we therefore model single and dual absorber devices where hydrogen (as a fuel) and valuable oxidation products are simultaneously produced. We discuss the effect of the thermodynamic potential and kinetics of the different oxidation reactions on the solar-to-hydrogen (STH) efficiencies of PEC devices and point out how new catalysts for partial oxidation of water to H2O2 will increase PEC efficiencies. Utilizing state of the art modelling approaches provided by a JavaScript, web based model (WBM) developed by Seger et al.[27] (www.SolarFuelsModeling.com), it will be demonstrated that bromine, chlorine and hydrogen peroxide based STH conversion efficiencies are high, and PEC technology might be economically viable.

The oxidation reactions considered in this study are summarized in **equations (1)-(3)**:

$2Br^- \rightarrow Br_2 + 2e^-$ $E^0 = 1.09$ V vs. RHE (1)

$2Cl^- \rightarrow Cl_2 + 2e^-$ $E^0 = 1.36$ V vs. RHE (2)

$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ $E^0 = 1.78$ V vs. RHE (3)

Of all these oxidation reactions, only the bromine evolution reaction (BrER, equation 1) is thermodynamically favored over the oxygen evolution reaction (OER, **equation 4**):

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = 1.23$ V vs. RHE (4)

Nevertheless, the $2e^-$ oxidation process of Cl_2 is favored if well-designed electrodes are used inducing a low overpotential for the Cl_2 production reaction, while still maintaining a

high overpotential for the thermodynamically favored OER (in acidic solutions).[31–37] BrER with only one reaction intermediate, can easily be kinetically favored as well.[38,39,10]

Using the WBM we have calculated solar-to-chemical/solar-to-hydrogen (STC/STH) efficiencies (for further information see SI) of different devices. The baseline parameters used to model these devices were chosen in agreement with previous work by Seger et al.[27] (see **Table 2** and SI **Table S1** and **Figure S1**). For BrER and ClER the parameters were modified to account for changes in overpotential, and ionic conductivity. (For further information about the parameters, see SI.) **Figure 1 a-b** indicate the obtainable STC/STH efficiencies for a PEC device containing a stacked, two-photon absorber, with the oxidation reactions being BrER (Figure 1a and **Figure S2**) and ClER. The corresponding STH efficiency considering OER is shown in Figure S1. With increasing thermodynamic potential of the aimed product, the STH gradually increases, i.e. for BrER a maximum STH of 19.65% can be obtained, whereas for OER and ClER, theoretical STH efficiencies of 22.05% and 24.45% can be achieved. The minimal necessary operating voltage for the BrER, OER and ClER devices at their maximum operating point is 1.48 V, 1.73 V, and 1.73 V respectively (see SI for further information). This analysis shows that even though the BrER reaction has a lower overpotential than the OER reaction, it actually is predicted to result in less efficient PEC devices. This peculiarity is rationalized by the definition of efficiency that relates to the chemical potential difference between reactants and products. When water is oxidized this difference is 1.23 V, whereas bromide ions are oxidized at 1.09 V. As noted by Vesborg and Seger, PEC reactions with operating potentials near 2 V are optimally suited to match the efficiency of 2-photon tandem PEC devices.[30] Given that the BrER reaction operates at 1.48 V, whereas both the OER and ClER operate at 1.73 V, it is clear that deviation from the optimal tandem device voltage significantly effects solar to hydrogen fuel production and the BrER efficiency is mitigated by the misalignment of the reaction operating potential with the optimal tandem device potential.

On the other hand, the choice of oxidation reaction only slightly affects the most suitable band gap combination of top and bottom cell absorber. For all cases the optimal top cell absorber should have a band gap of E_{top} = 1.78 eV. To construct a PEC device with the highest STC efficiency a matching bottom cell absorber with a band gap of E_{bot} = 0.68 - 0.94 eV (with the narrowest range of (E_{bot} = 0.92 – 0.94 eV) for the OER) should be used. The lower voltage needed for the BrER also means that for most band gap combinations the device will be limited by photocurrent, rather than photovoltage. While at top cell band gaps above ~1.75 eV, the top cell is providing the limiting photocurrent, at top cells below ~1.75 eV the bottom cell is providing the limiting photocurrent. Figure 1c allows for the top cell photoabsorber to be thinned to optimize photon matching between both photoabsorbers. (The corresponding percentage of thinning is shown in Figure 1d). This greatly expands the region of highly efficient devices, and allows the use of Si bottom cell absorbers with various top cell absorbers. Si is highly efficient and a well-studied material in PEC water splitting. The same top cell thinning approach was also calculated for the ClER (Supporting Information, **Figure S3**) with a slightly smaller positive effect.

Simulated STC efficiencies for PEC devices calculated with more dilute electrolytes are shown in **Figure S4**. For HBr, decreasing the concentration to 0.1M does not affect the maximum efficiency, decreasing the concentration to 0.01M HBr drops the efficiency by 7%. Hence, electrolyte induced losses are negligible compared to other losses for electrolyte concentrations above 0.1M. Below 0.1M HBr ionic losses start to dominate.[40]

PEC devices that produce hydrogen peroxide (**Figure 2**) are characterized by a thermodynamic redox potential significantly more oxidative than the OER (1.78 V compared to 1.23 V for OER). This makes selective H_2O_2 production experimentally challenging. Nevertheless, selective production of hydrogen peroxide by oxidation of water was recently reported to occur on carbon materials and MnO_x,[15,16] with these catalysts typically achieving a 40% faradaic efficiency. Since these oxidation catalysts need basic conditions, the PEC

modelling was done using either 0.1M or 1M KOH with HER overpotentials slightly worse than our previous reactions done in acid (η_{HER} = 35 mV[41] @ 1 mA/cm^2 with a Tafel slope of 40 mV dec^{-1}). The hydrogen peroxide overpotential (η_{H2O2}) losses were fixed (150 mV[16] and 350 mV). Otherwise the same conditions as for BrER and ClER were used.

Figure 2a displays the STC efficiencies for three different conditions assuming that catalytic/engineering improvements can increase the faradaic efficiency for oxidative hydrogen peroxide production to 100%. *In reality, e.g. in cases where hydrogen peroxide is produced with lower FE mixtures of oxygen and hydrogen peroxide are produced. Hence, the resulting STC will be based on two different thermodynamic potentials, e.g. for OER and H_2O_2. To achieve a good comparability between the different processes 100% FE for H_2O_2 was used as similar FE can be achieved for BrER, ClER, and OER, respectively.* In general, all conditions allow high STC, with Figure 2a showing a maximum of up to 27.55% for a 1.87 eV/1.24 eV bandgap combination assuming low overpotentials and a highly basic environment. This STC efficiency is quite high, due to the optimal operating potential near 2 V (see SI for further information). Given that to date no catalyst providing faradaic efficiency of 100% for the selective 2-electron oxidation of water to hydrogen peroxide is known, it should be emphasized that finding a good catalyst driving this reaction with high selectivities is one of the challenges that should be addressed. Still, even with sub-optimized STC efficiencies, this might be quite an economically promising approach given the value of H_2O_2, as well as realizing that H_2 produced in this device would still be running at 100% FE.

Figure 2b shows that a 200 mV increase in catalytic losses only decreases the efficiency slightly to 25.32 %. However, switching to 0.1M KOH decreases the efficiency much more drastically to 21.8%. Si (E_g =1.12 eV) would be a well-suited bottom cell. For the conditions used in Figure 2b and 2c, i.e. higher overpotential and lower electrolyte conductivity, the optimal bottom material requires a high band gap; a property of e.g. (expensive) GaAs. In Figure 2d, the contour plot obtained for top cell ‘thinning’ is shown

(**Figure S5** shows the 'thinning %' of the top cell absorber). From these data it is obvious that for a tandem device consisting of two stacked materials with similar band gap of 1.55 eV, 'thinning' results in an increased (as well as total) STC efficiency of 19.7%. Considering two stacked GaAs cells (band gap of $E_g \approx 1.42$ eV) STC efficiencies greater than 10% can be achieved by 'thinning' down the top cell absorber by ≈ 52%. Given that GaAs produces much better photovoltages than the model used, the actual efficiency could likely be even higher.[42] For materials prepared by epitaxial growth this approach might reduce the cost significantly.

An interesting point discovered with PEC water splitting is that while the highest potential efficiency can be obtained with a two-photon tandem photoelectrochemical (PEC) device, [23,24,11,25,26] recent techno-economic analysis suggests that a single absorber approach utilizing a semiconductor with a large band gap is more feasible in terms of price per kg of hydrogen.[19,20] The authors clearly show that the capital costs for the implementation of hydrogen production facilities using a PEC tandem device approach are circumventing economical hydrogen production from water. Instead a slurry based particle approach with one photon absorber might be more suitable as capital costs can be significantly reduced compared to tandem approaches.[19,20] **Figure 3** investigates the approach of a single photoabsorber for BrER, ClER and H_2O_2 by modelling the STC efficiencies using the same parameters as in Figure 1 and 2, i.e. faradaic efficiencies of 100%.

In comparison to the tandem approach, the order in STC efficiencies is different, with HBr splitting being significantly more efficient than HCl or water-splitting. For HBr splitting applying an optimal single absorber with a band gap of 1.78 eV, STC efficiencies of 18.9% could be achieved exceeding the maximum efficiency of 19.03% for a dually stacked absorber device. This can be attributed both to the lower thermodynamic potential, as well as to the low bottom cell. In tandem devices the efficiency of the bottom cell is hampered by low energy photon absorption of the electrolyte.[30] For single-cell absorbers, reactions with operating potentials near 1 V are optimally suited to achieve high efficiencies, as is the case for HBr

splitting. The high efficiencies calculated here for single band gap absorbers in HBr splitting are in good agreement with results obtained by McFarland et al,[10,43] proving the suitability of efficient single cell absorber devices. As can also be seen from Figure 3, higher STH efficiencies can be obtained for water and HCl splitting in tandem devices, as compared to single cell absorbers, due to the higher operation potential required to drive these reactions. Finally, the data suggest that hydrogen peroxide production with a single absorber is relatively inefficient with an STC of 6.2% and is less suited for large-scale solar hydrogen production.

Conclusions and further remarks

Photoelectrochemcial splitting of water is considered a promising route to a hydrogen based economy, however strong economic barriers are impeding its implementation. While costs will decrease with improving performance,[15] in this work we show the feasibility of co-production of valuable chemicals such as halides or H_2O_2 concominant with H_2 production to boost PEC implementation. By doubling the amount of valuable products we can help decrease the economic barrier preventing solar H_2 from entering the market. While halides and/or H_2O_2 market is minimal in comparison to the H_2 market, it is still large enough to allow for the development of the desperately needed photoelectrochemistry industry. *It is anticipated that the high value of the oxidation products considered in this study might also allow to build devices with lower STC/STH efficiencies. Still a detailed techno-economic feasibility study is required to support this assumption*

Nevertheless, based on the modelling results presented in this perspective, solar-to-hydrogen efficiencies producing Br_2, Cl_2, or H_2O_2 are as high, or even higher than for similar devices when producing O_2. The low thermodynamic potential for HBr allows for efficiencies from a single photoabsorber on par with that of a tandem device. Here only Pt-based HER

catalysts were considered, but materials with higher stability, i.e. with higher corrosion resistance or lower tendency for halide adsorption,[39] should be used in an actual device. *For the devices discussed in this manuscript still several challenges need to be addressed before a successful implementation can be realized: As for PEC water splitting the lifetime of the device is a crucial factor and the harsh conditions used in these processes (but also in PEC water splitting) suggest that protection layers are used to limit the corrosion of the light-absorbing semiconductor. For devices producing hydrogen peroxide catalyst development and testing is required as to date selective electrocatalysts for oxidative hydrogen peroxide generation are not known.*

Besides the presented approaches, there might be other reaction combinations of interest for construction of economically viable solar-to-chemical production devices. In particular, devices producing hydrogen peroxide by two-electron reduction of oxygen, coupled to two-electron water oxidation to H_2O_2 should be considered.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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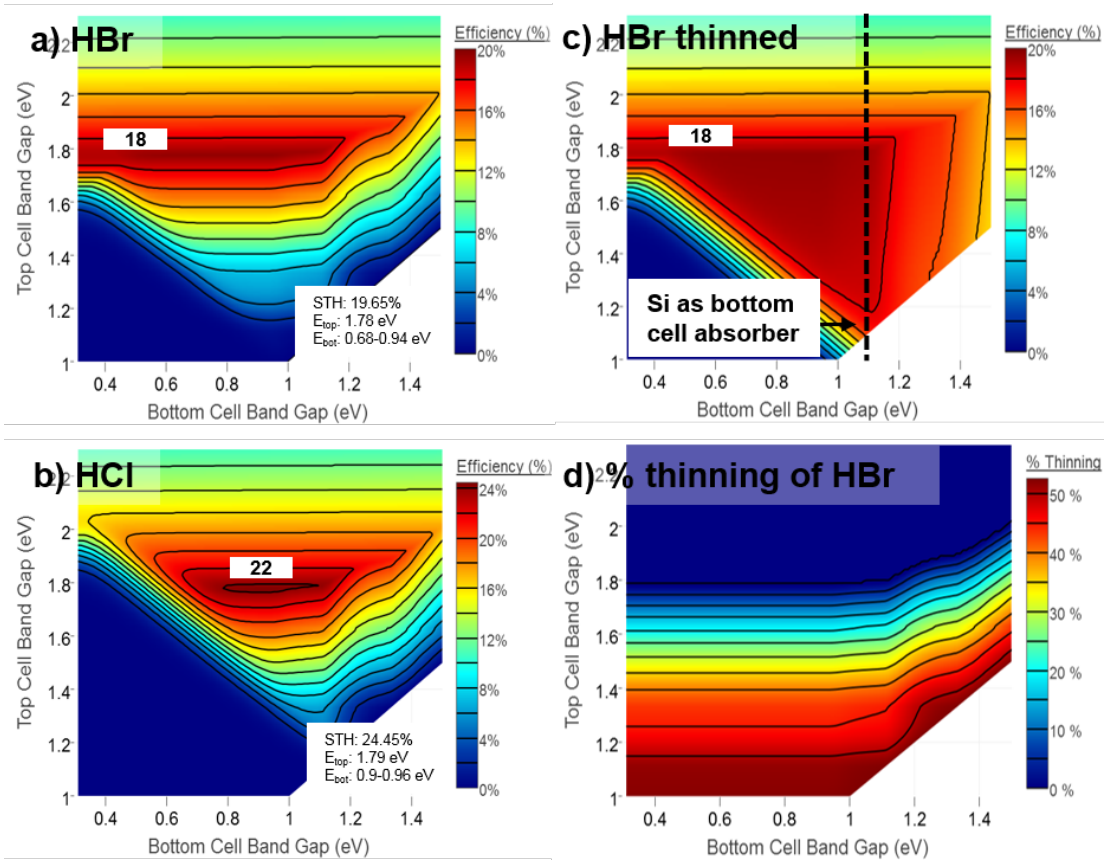

Figure 1. Maps of theoretical tandem PEC efficiency limits for HBr, and HCl based hydrogen production devices a-c). The STH efficiency calculations were performed using the WBM[26] . a) and b) were calculated using kinetic parameters as shown in Table 2, allowing light absorption by a thin water film. In c) current matching by top cell absorber thinning is allowed to mitigate limitations by the bottom cell. d) shows the corresponding thinning values to achieve the STH values presented in c).

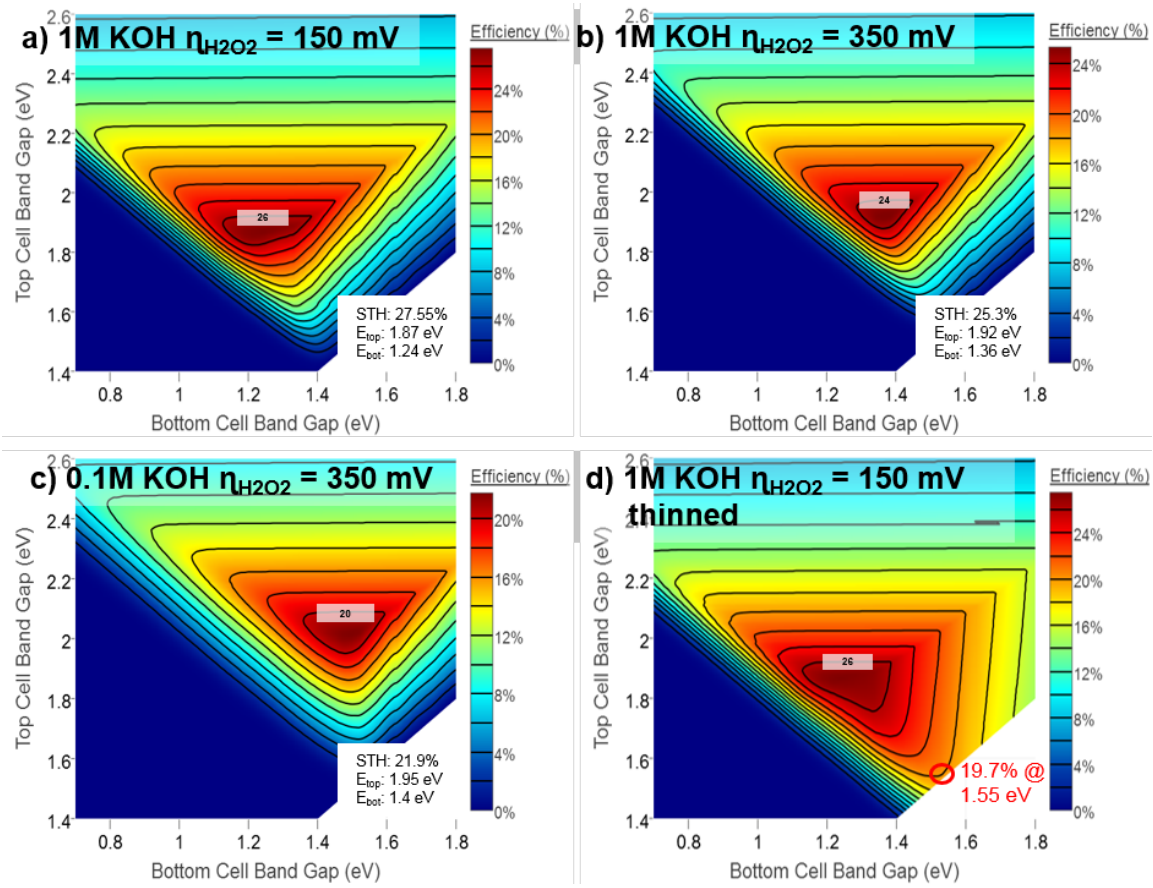

Figure 2. Maps of theoretical tandem PEC efficiency limits for water splitting to produce hydrogen and hydrogen peroxide. The contour plots were calculated for different overpotentials for the H_2O_2 production. The same parameters as in Figure 1 were used except that KOH was used as electrolyte, the overpotential for 2-electron water oxidation was fixed (150 mV and 350 mV), and a thermodynamic potential of 1780 mV were used.. a) for a device where 150 mV additional overpotential are required for the H_2O_2 production in 1M KOH, b) for a device where 350 mV additional overpotential are required in 1M KOH, and c) for a device where 350 mV additional overpotential are required and 0.1M KOH is used. d) Thinning of the top cell absorber was allowed for the conditions used in a). Very efficient devices can be created with band gaps of E_g = 1.55 eV when thinning of the top absorber is allowed.

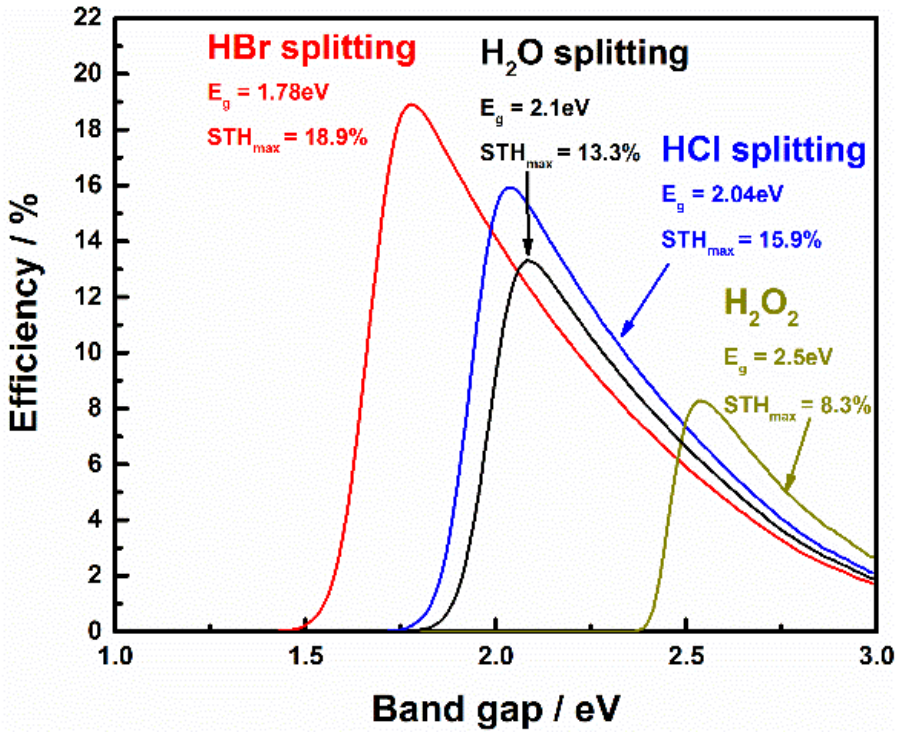

Figure 3. Plot of STC efficiency for single band gap absorber for the baseline cases used to calculate the dual absorber devices, i.e. 100% FE.

Table 1. Selection of valuable electrochemical oxidation products.

Product	Price ($/ton)	Annual Production (tons/y)
H_2	1400 [18]	1.2 x 10^7 (refinery capacity) [d]
Cl_2	230-500 [a]	56 x 10^6 [e]
Br_2	3400 [b]	0.56 x 10^6 [e]
H_2O_2	500-1200 [c]	3.8 x 10^6 [e]
O_2	35	-

Data for the prices of Cl_2, Br_2 and H_2O_2 are adapted from [a] www.vci.de; [b] http://www.sunsirs.com/; [c] www.icis.com/chemicals (data are from 2006 and a significant increase in market price can be expected). The annual production was adapted from [d] http://hydrogen .pnl.gov/hydrogen-data/refinery-hydrogen-production-capacities-country; [e] www.essential-chemicalindustry.org/chemicals (all sites were accessed 3-8-2016).

Table 2. Simulation parameters for the modelling of the electrochemical parameters of hydrogen HER, bromine BrER, and chlorine ClER evolution reaction.

Symbol	Explanation	Value
η_{HER}	Overpotential (HER[25,41])	25 mV @ 1 mA cm^{-2} 30 mV dec^{-1}
$\eta_{BrER/ClER}$	Overpotential (BrER[9]/ClER[32–34])	25 mV @ 1 mA cm^{-2} 40 mV dec^{-1}

Co-production of valuable chemicals such as halides or hydrogen peroxide concomitant with hydrogen production are presented as a strategy to boost the industrial applicability of photo-electrochemical and photo-catalytic systems. Highly efficient two-photon devices can be fabricated (solar-to-chemical efficiencies of > 27%), whereas single absorber devices will be appropriate for e.g. HBr splitting and efficiencies of almost 19% can be obtained.

Solar fuels

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Beyond water splitting - efficiencies of photoelectrochemical devices producing hydrogen and valuable oxidation products